International Communications in Heat and Mass Transfer 94 (2018) 24–31

Contents lists available at ScienceDirect

International Communications in Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ichmt

Development of nanoemulsion CO_2 absorbents for mass transfer performance enhancement

Seonggon Kim[a], Myunghwan Jeong[a], Jae Won Lee[a], Sae Young Kim[a], Chang Kyoung Choi[a,b], Yong Tae Kang[a,*]

[a] School of Mechanical Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea
[b] Department of Mechanical Engineering-Engineering Mechanics, Michigan Technological University, Houghton, MI 49931, USA

ARTICLE INFO

Keywords:
CO_2 absorbents
Dispersion stability
Dodecane
Nanoemulsion
Surfactants
Thermophysical properties

ABSTRACT

Nanofluids as CO_2 absorbents have problems involving precipitation or flocculation of the seeding particles. Nanoemulsion CO_2 absorbents are expected to solve these problems. In this study, nanoemulsion (Dodecane/Methanol) absorbents were proposed and their thermophysical properties and dispersion characteristics were evaluated for mass transfer performance enhancement during CO_2 absorption process. Both Span 60 and Tween 60 were selected due to their nonionic surfactant feature and hydrocarbon chemical types of dodecane. The nanoemulsion absorbents were ultrasonically manufactured after adding Span 60 and Tween 60 in a ratio of 4:6 to match the required hydrophile-lipophile balance (HLB = 11). Thermal conductivity and viscosity of nanoemulsion absorbents were measured for various surfactant ratios. Tyndall effects and turbidity measurements were executed to find out the best dispersion stability condition. An optimal ultrasonication time was proposed based on the smallest mean size of nanoemulsion droplets and their uniformity. Both mechanisms of thermophysical properties and dispersion stability of nanoemulsion absorbents were proposed based on cryo transmission electron microscope (TEM) results.

1. Introduction

The rapid increase in the world's energy consumption has forced researchers to look for more efficient uses of oil and electricity [1]. The integrated gasification combined cycle (IGCC) has emerged as one potential/partial solution [2]. However, there is a severe problem of CO_2 discharge because the IGCC has to use coal to generate energy [3]. There are three methods employed to capture this CO_2: adsorption, membrane, and absorption [4–6]. The adsorption method using a solid adsorbent has the highest performance, but it requires the highest energy consumption for regenerating adsorbents. In addition, it is not suitable in a humid environment and for a large-scale facility as this adsorbent has no fluidity [7,8]. The membrane method uses a separation feature due to their different transmittances, which does not require a regeneration process. It is suitable when CO_2 is at high pressures and high concentrations. However, it is not applicable for the large-scale process because of high equipment costs [9,10]. On the other hand, the absorption method not only has a high CO_2 capture performance but also easily regenerates the absorbents by heating or decompressing [7]. Since the absorption method uses a liquid solvent of a high fluidity, it is easy to be applied as an actual process compared to other methods.

CO_2 can be absorbed chemically or physically. The chemical absorption method using chemical reactions performs well and is suitable under atmospheric pressure and temperature conditions. However, this method requires high energy consumption to regenerate absorbents [11,12]. On the other hand, the physical method is a solubility-based absorption that is more suitable for higher pressures and higher concentrations of CO_2. It needs less energy to regenerate absorbents than the chemical absorption process [11]. In addition, the physical absorption method is the cheaper and does not require additional materials to avoid toxicity and corrosiveness that is required by the chemical method [12]. The physical absorption method is the most preferable in the IGCC process due to the conditions of high pressure, high CO_2 concentration, and high capacity. Especially, the rectisol process, as a representative physical process, deals with syngas, and since methanol is used as an absorbent, the equipment cost is much lower than other absorption processes. Moreover, the rectisol process absorbing CO_2 gas selectively does not deteriorate the overall efficiency. It is, therefore, suitable for use in the IGCC process dealing with syngas. However, a rectisol process must operate at a low temperature of −40 °C to achieve the desired absorption rate [13,14], which requires a large amount of

---

* Corresponding author.
E-mail address: ytkang@korea.ac.kr (Y.T. Kang).

https://doi.org/10.1016/j.icheatmasstransfer.2018.03.012

Nomenclature		*Subscripts*	
HLB	Hydrophile-lipophile balance	k	Thermal conductivity, W/m·K
NTU	Nephelometric turbidity units	A	surfactant A
x	Mass fraction	B	surfactant B
E	Enhancement coefficient	ne	nanoemulsion
k	Thermal conductivity, W/m·K	b	base fluid

consumption during the cooling process. Thus, a CO_2 absorbent that can be used at room temperature with absorption performance increased is expected to save energy and cost [15].

Nanofluids, as a new absorbent, consisting of solid nanoparticles in methanol are developed to improve CO_2 absorption. It has been reported that Al_2O_3, SiO_2, and Fe_3O_4 nanofluids improve the absorption performance of CO_2 [16–19]. However, there is a serious problem of particle aggregation. Also, it is easy to precipitate due to higher densities [20]. The precipitated particles adhere to the surface of the tube, causing corrosion as well as flow impediment. In order to solve these problems, nanoemulsion absorbents have been developed by adding immiscible liquid droplets instead of solid nanoparticles into the base fluid. The nanoemulsion absorbent has advantages of high dispersion stability, no corrosion, and no tube clogging. Most conventional nanoemulsion use water as a base fluid [21,22]. In this study, we have developed methanol-based nanoemulsion, named as a “nanoemulsion absorbent” in this study for CO_2 capture applications. After selecting appropriate surfactants considering the chemical properties and necessary hydrophile-lipophile balance (HLB) requirement, thermophysical properties and dispersion stability of the nanoemulsion absorbents are evaluated in terms of surfactant ratios. In the final analysis, an optimum ratio of surfactants is chosen, and relevant mechanisms of dispersion and thermal properties of CO_2 nanoemulsion absorbents are suggested.

2. Method and rationale

2.1. Preparation of nanoemulsion absorbents

As shown in Fig. 1, dodecane is added to 350 ml of pure methanol, and the stirring and the ultrasonication are performed for 30 min to form sufficiently dispersed small droplets in the methanol. Various volumes of Span 60 and Tween 60 are added to 100 ml of pure methanol and stirring was carried out for another 30 min. After the mixture of dodecane/methanol and the mixture of surfactant/methanol are added, stirring and ultrasonication are performed for 2 h to allow the surfactant to act as a coating for the dodecane droplet. The dodecane is also divided into nano-sized droplets to form a nanoemulsion. During the manufacturing process, the temperature of the absorbent is maintained at 20 °C using a constant temperature water bath. For the preparation of the nanoemulsion absorbent, a 20 kHz, 750 W ultrasonicator is used. The amount of dodecane and surfactants added in the preparation of the nanoemulsion absorbents is determined according to the conditions in Table 1.

Dodecane is chosen because it does not react with the methanol that is used for the base fluid. In addition, the three factors are considered in the selection process - density, viscosity, and thermal conductivity. Larger density oils than methanol have a higher probability of sedimentation, which may interfere with the uniform dispersion. Alternatively, if the density of oil is low, they will easily rise to the surface, which may cause phase separation. The density of dodecane is 750 kg/m^3, similar to methanol of 792 kg/m^3, so that sedimentation and phase separation do not easily occur. In addition, the thermal conductivity of dodecane is 0.140 W/m·K, which is greater than that of the silicone oil (0.100 W/m·K) used in the previous study [23]. Therefore, dodecane is favorable for heat transfer and mass transfer performance. Also, the dodecane viscosity is 1.34 mPa·s, a value that is low among oils. This lower viscosity requires less power consumption during the CO_2 absorption process. Also, the lower the viscosity is, the smaller the dispersed droplets diameter which creates more stable nanoemulsions [24].

Both Span 60 and Tween 60 (polyoxyethylene sorbitan fatty acid esters) are selected by considering hydrocarbon chemical types of dodecane and the fact that dispersion stability of mixed surfactants is better than single surfactants [25,26]. Span 60 and Tween 60 are mixed at a ratio of 4: 6 to match the required HLB of 11. The HLBs of Span 60 and Tween 60 are 4.7 and 15.6, respectively. Ratios of surfactants are calculated using the following Eq. (1);

$$\mathrm{HLB}_{blended} = \frac{(x_A * HLB_A + x_B * HLB_B)}{x_A + x_B} \tag{1}$$

2.2. Evaluation of thermophysical properties

Viscosity is a property that directly affects the power consumption required for the CO_2 absorption process. The higher the viscosity, the

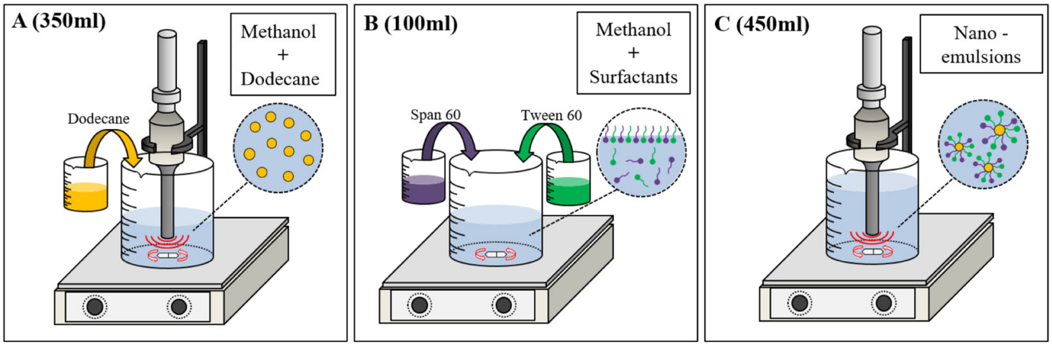

Fig. 1. Manufacturing method of nanoemulsion absorbents. A: Add a certain amount of dodecane to methanol. Stirring and ultrasonication are carried out for 30 min to disperse the dodecane droplets to small size. B: At the same time as the A process, both Span 60 and Tween 60 are added to 100 ml of methanol at a 4:6 ratio, and stirring is continued for 30 min. C: After combining the mixtures formed in process A and B, stirring and ultrasonication are carried out for 2 h, so that the surfactant sticks to the droplets and a nano sized droplets are formed.